

Development of High Temperature Membranes and Improved Cathode Catalysts

Dr. Sathya Motupally

UTC Fuel Cells (UTCFC)

195 Governor's Highway

South Windsor, CT 06074

Phone: (860) 727-7175; E-mail: Sathya.Motupally@UTCfuelcells.com

DOE Technology Development Manager: Valri Lightner

Phone: (202) 586-0937; Fax: (202) 586-9811; E-mail: Valri.Lightner@ee.doe.gov

Subcontractors:

High Temperature Membrane:

Virginia Polytechnic Institute and State University, Blacksburg, VA

Pennsylvania State University, University Park, PA

Stanford Research Institute International, Menlo Park, CA

IONOMEM, Marlborough, CT

Princeton University, Princeton, NJ

Cathode Catalysts:

Northeastern University, Boston, MA

University of South Carolina, Columbia, SC

United Technologies Research Center (UTRC), East Hartford, CT

Case Western Reserve University, Cleveland, OH

Objectives

- Develop and demonstrate an advanced polymeric membrane able to operate at near ambient (1-1.5 atm.) pressure in the temperature range of 120~150°C that is able to meet DOE goals for performance.
- Develop and demonstrate improved Pt cathode catalysts that will enable the reduction of Pt loading to 0.05 mg/cm² and meet DOE goals for performance.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year R,D&D Plan:

- P. Durability
- Q. Electrode Performance
- R. Thermal and Water Management

Approach

- **Phase 1:** High temperature membranes (HTMs) and improved Pt catalysts will be synthesized, characterized and compared with issued specifications. [In progress]
- **Phase 2:** Laboratory-scale catalyst-coated membranes (CCMs) will be fabricated, optimized and tested using the Phase 1 down-selected membranes and catalysts.
- **Phase 3:** Full-size CCMs with the down-selected and optimized HTMs and catalysts will be fabricated and tested in 2 individual multi-cell stacks.

Accomplishments

This project was initiated during the first quarter of 2002. The down-selection to retain promising catalysts and HTMs is scheduled for Q3 of 2003. All subcontractors are working towards optimizing their respective catalyst and HTM systems.

- Four membrane systems with proton conductivity on the order of 10 mS/cm at 120°C and 50% relative humidity (RH) were synthesized:
 - Biphenyl sulfones (BPSH) from Virginia Tech,
 - Modified sulfonated polyetheretherketone (S-PEEK) from Stanford Research International,
 - Fluorinated polyether sulfone (FPES) from Penn State, and
 - Heteropolyacid (HPA) filled Nafion® from IONOMEM.
- IONOMEM has established a baseline for HTM performance of 0.6 V at 0.4 A/cm² (120°C, 30% RH).
- Slab band calculations using Vienna ab-initio slab program (VASP) project have provided insight into binary alloy skin effect.
- Higher activity and more stable binary Pt alloys were synthesized using the colloidal-sol, carbothermal, and pulse electrodeposition routes.
- Reproducible and state-of-the-art (SOA) CCMs were fabricated using the decal transfer process.
- All the requisite details and infrastructure for the catalyst and membrane down-selection process have been established. The down-selection process will commence during Q3 of 2003 and will be completed by the end of Q1 of 2003.

Future Directions

- Further optimize membrane systems and/or fillers required to improve conductivity at practical RH.
- Develop a generalized stability template for HTMs.
- Continue Pt-alloy synthesis using the various routes and optimize for activity and stability.
- Investigate several methodologies to reduce Pt loading (e.g., ionomer gradient, etc.).
- Initiate catalyst and HTM down-select process.

Introduction

Two main challenges in the proton exchange membrane (PEM) fuel cell arena are the reduction of cathode Pt loading and development of membranes that can operate over 120°C. Surmounting these two challenges will directly affect the cost, performance and the size of PEM fuel cell stacks. On the HTM project, new polymeric materials with negligible thermal degradation and acceptable proton conductivity in the 120-150°C range are required. On the improved catalyst project, a combination of higher activity catalysts and thinner catalyst layers is required to achieve the aggressive DOE performance targets.

Approach

To develop HTMs, UTCFC has teamed with research groups that possess competencies in the field of polymer chemistry and engineering. The subcontractors on the project are investigating modified Nafion® and new non-Nafion based membrane systems (see Table 1). The subcontractors on the improved catalyst project and their individual approaches are given in Table 2. More details on both the approaches can be found in Reference.

Results

This project was initiated in June of 2002. Since then, all the subcontractors on the project have set up

the necessary infrastructure and have reported significant progress in the areas of catalyst and polymer synthesis. New catalyst systems with improved activity and stability relative to commercial pure Pt carbon supported systems have been identified. Under the HTM program, UTCFC has stressed the importance of developing polymers capable of conducting protons under practical relative humidity (RH) conditions. The HTM subcontractors are optimizing their polymeric materials for acceptable proton conductivity at 120°C and 50% RH. A number of polymer systems whose proton conductivities are on par with or exceed that of Nafion® have been identified. Salient progress details are presented below.

High Temperature Membrane: On the HTM project, four of the five subcontractors have successfully synthesized polymer systems that yield finite proton conductivities at 120°C and 50% RH. One issue faced by most of the polymer subcontractors has been poor conductivity for their membrane systems at practical RH conditions. Prior to Q2 of 2003, polymer membranes solely constituted by a

blend of the basic sulfonated monomer showed excellent proton conductivity at 120°C and saturated conditions. However, the conductivity dropped off steeply as the RH was lowered below 100%. To overcome this issue and to minimize the dependence of the membrane proton conductivity on the humidity, all the subcontractors have tested the addition of hydrophilic conductivity enablers. These hydrophilic additives improve the water retention capability of the polymers at low RH. The types of fillers investigated to date include a wide variety of inorganic heteropolyacids and proprietary hydrophilic polymeric blends. With the aid of the the above types of fillers, the HTM subcontractors have consistently measured a proton conductivity greater than or equal to 0.03 S/cm (reference point of Nafion 117) at 120°C and 50% RH.

An example of one class of filled polymers that shows good promise is the fluorinated sulfonated polythetheretherketone (FSPEEK) from SRI International (see Figure 1 for a schematic of the basic polymer). The sulfonated polymer is blended with a basic polymer to generate pseudo-crosslinking through an acid-base interaction, thus providing

Table 1. High Temperature Membrane Project Approach

Group	Principal Investigator	Approach
IONOMEM	Mr. Leonard Bonville	Hygroscopic solid ion conductor (e.g., zirconium phosphate, etc) filled Nafion®
Penn State University	Prof. Digby Macdonald	Sulfones and sulfoxides of aromatic PPBP and aliphatic PVA. Covalent sulfonic acid bonded PEEK, PBI and PPBP
Princeton University	Prof. Andrew Bocarsly	Layered sulfonated Polystyrene/Fluoropolymer system
Stanford Research Institute	Dr. Susanna Ventura	Sulfonated PEEK-PBI-PAN
Virginia Tech	Prof. James McGrath	Sulfonated Poly(arylene ether sulfone)

Table 2. Advanced Cathode Catalyst Project Approach

Group	Principal Investigator	Approach
North Eastern University (NEU)	Prof. Sanjeev Mukerjee	Micellar Pt nano cluster synthesis, colloidal sol synthesis of binary Pt alloys.
University of South Carolina (USC)	Prof. Branko Popov	Pulse electro-deposition of Pt and Pt alloys on Carbon. [Pt and Pt-X, X=Fe, Ni, Co, Mn and Cu]
UTC Fuel Cells (UTCFC)	Mr. Michael Perry	Carbothermal synthesis of ternary Pt alloys. [Pt-Ir-X and Pt-Rh-X, [X =Ni, Co and V]]
Case Western Reserve University (CWRU)	Prof. Alfred Anderson	Quantum chemical modeling of Pt alloys and ORR.
UT Research Center (UTRC)	Dr. Ned Cipollini	Reproducible and stack size CCM fabrication.

conducting polymer membranes with good mechanical stability. To minimize the dependence of the membrane proton conductivity on the humidity, SRI has tested two classes of hydrophilic polymers. Figure 1 illustrates the proton conductivity of several SRI polymer membranes at 120°C as a function of the RH. The conductivity of Nafion 117 (blue diamond) is shown as a reference line. The black line (hollow squares) shows the proton conductivity of the first-generation SRI membrane, where no additive was used in the polymer blend of the acidic/basic polymer. The conductivity of this membrane drops quite significantly at RH lower than 80%. On the other hand, membranes containing hydrophilic polymer additives (14210-21c, 14210-25, and 14210-53) showed significantly higher conductivity at low RH than the correspondent membrane without any additives. In particular, the conductivity at low RH for these membranes was found to be higher for additives with higher hydrophilic character. The SRI membrane 14210-53 was found to have the highest conductivity at 30 and 50% RH. For this membrane, proton conductivity values were 0.011 S/cm at 120°C and 30% RH and 0.038 S/cm at 120°C and 47% RH. These conductivities were higher than any other SRI membranes, as well as higher than Nafion 117.

A summary of proton conductivities of other membrane systems developed under this project is

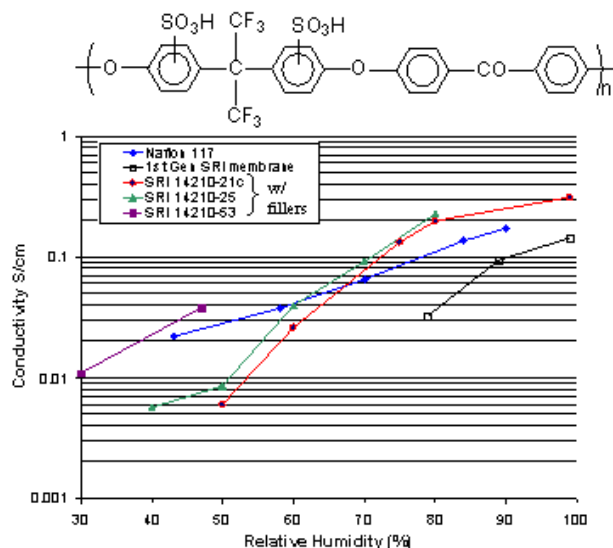


Figure 1. Conductivity Measured at 120°C as a Function of RH for Polymer Membranes with Variable Composition (blue [diamond] line: Nafion 117)

shown in Figure 2. The 120°C and 50% RH proton conductivity metrics for biphenyl sulfones (BPSH) filled with hetero-polyacid from Virginia Tech., FSPEEK from SRI International, fluorinated polyethersulfones (FPES) from Penn State and Nafion filled with hetero-polyacid from IONOMEM are presented in the figure. The conductivity values of the membranes are compared to that of Nafion 117. As seen from the figure, the conductivities of all the membrane systems on the project are higher than the corresponding Nafion value. It is also important to note that the glass transition temperatures of the membranes shown in Figure 2 are higher than Nafion. Prior to the down-select process, the membrane subcontractors are further optimizing the thermal, mechanical and chemical stability of the membranes.

Reproducible and SOA high temperature fuel cell performance has been established by IONOMEM. The IONOMEM technical approach for high temperature catalyzed membranes integrates, on a molecular level, the proton-conducting Nafion® polymer with hygroscopic hetero-polyacids such as phosphotungstic acid, or zirconium hydrogen phosphate. This nano-composite material maintains low water vapor pressure, provides more water-independent proton conduction, and holds promise of satisfying DOE

Summary of membrane conductivity

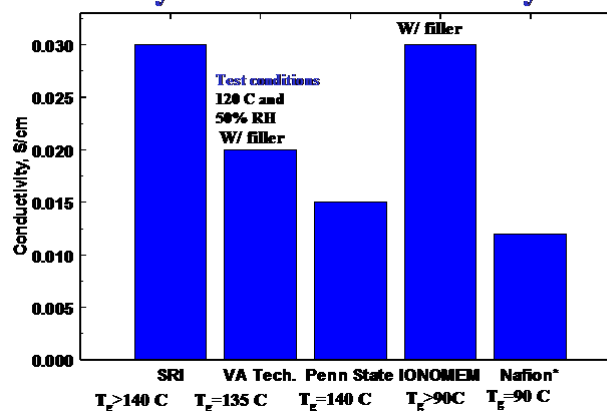


Figure 2. Summary of Proton Conductivities Measured at 120°C and 50% RH by the Various Subcontractors on the HTM Project (see Table 1, SRI: FSPEEK, VA Tech.: BPSH, Penn State: FPES, IONOMEM: Nafion filled with hetero-polyacid)

performance requirements. At the project initiation, IONOMEM's high-temperature membrane electrode assembly (MEA) demonstrated a consistent performance level of 0.454 volts at 400 mA/cm², operating at 120°C and ambient pressure on hydrogen and air both saturated near 90°C. The performance under the above-mentioned conditions was further enhanced to 0.6 V at the same current density during 2003. Polarization curves at 120°C and 35% RH for the IONOMEM membrane are shown in Figure 3. As seen from the Figure, the 400 mA/cm² performance at 120°C and 35% RH (albeit at low fuel and air utilizations) is 600 mV. The corresponding ohmic resistance at 120°C and 35% RH is 0.18 ohm-cm².

Advanced Cathode Catalysts: The advanced catalyst project is set up with three of the four subcontractors (Northeastern University, University of South Carolina, and UTCFC) synthesizing more active Pt alloy catalysts. Case Western Reserve University (CWRU) is supporting the catalyst synthesis task with fundamental molecular level simulations, and UTRC is fabricating and testing MEAs using the catalysts synthesized on the project.

CWRU's main goal on this project is to gain understanding of structure and electronic factors in oxygen electroreduction over platinum alloyed with transition metals. Their approach has been to predict, using quantum mechanical calculations, the reversible potentials for water oxidation on platinum alloys to form adsorbed OH, the surface species that

is believed to block oxygen from reaching the electrode surface (Reference 2). During Q2 of 2003, Case completed calculations of H₂O and OH bonding to various sites on the four layer slab models of the (111) Pt₃Cr surface with and without a monolayer Pt surface "skin" which is found to form on supported alloy particle catalysts and on single crystal alloy surfaces (Reference 3). They found that their predictions for the Pt skin effect were in good agreement with the shift in overpotential for O₂ reduction and the apparent shift in onset potential for H₂O(ads) oxidation to OH(ads) seen in the literature for Pt₃Cr and other Pt alloys with metals from the first transition series. These results are currently being applied by UTCFC to develop novel shell-core structures for superior oxygen reduction activity.

At UTCFC, in the ternary alloy area, we have completed the preparation and screening of Pt₇₅Ir_{12.5}X_{12.5} (X=Co, Ni, V) alloy systems using the carbothermal synthesis route (Reference 4). Electrochemical surface areas of the synthesized catalysts were in the 50-60 m²/g range with particle size in the 2-5 nm range. Half-cell activity measurements indicate that the catalyst activities of Pt alloys are in the order of Pt₇₅V₂₅ > Pt₇₅Ir_{12.5}V_{12.5} > Pt₇₅Co₂₅ > Pt₅₀Ir₂₅V₂₅ > Pt₇₅Ir_{12.5}Ni_{12.5}. The activity of Pt₅₀Ir₂₅V₂₅ was 1.7 X greater than pure Pt catalyst. This could result in a kinetic improvement of 15 mV at 65°C. X-ray diffraction analysis confirms that Pt₅₀Ir₂₅Co₂₅ and Pt₅₀Ir₂₅V₂₅ are ordered, face-centered cubic structures with reduced Pt-Pt near-neighbor distance, which might be the reason that their activities are superior to pure Pt catalyst. The path forward for UTCFC is to scale up the best catalysts in a large quantity (>20 g) for further evaluation in subscale cells.

In the binary alloy area, UTCFC has tested ca. 50% weight loading Pt-Co catalysts and compared the performance, endurance and cyclic durability with pure Pt. Figure 4 contains the comparison of the Tafel plots obtained in a subscale cell for Pt-Co and Pt. Analysis of the Tafel plots shows that the ratio of the volumetric exchange current densities of Pt-Co and Pt is 1.25. The ratio of the surface area of the Pt and Pt/Co catalysts is approximately 1.75 (obtained using cyclic voltammetry). Therefore, the ratio of the true catalytic activity is approximately 2.2. The increased catalytic activity translated to an increase

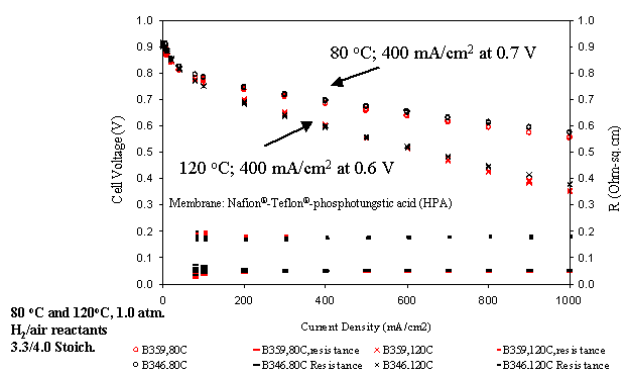


Figure 3. IONOMEM's High Temperature Fuel Cell Performance at 120°C and 35% RH (The performance is compared to performance under 80°C and saturated conditions.)

of ca. 10 mV at all current densities on the polarization curve. The stability of Co in the Pt-Co catalyst was investigated using electron microprobe analysis (EMPA) after 4000 cycles between 1.2 and 0.8 V. In Figure 5, the scans are compared to those obtained with pure Pt cycled under the same conditions as above. The EMPA scans show no migration of Co into the membrane or to the anode side. The absence of Co migration is a strong benefit for the Pt/Co alloy system.

Also, comparing the Pt dissolution fronts for Pt and Pt-Co catalysts shows that the Co incorporated into the catalyst stabilizes the Pt and reduces the rate of migration of the dissolved Pt.

At the University of South Carolina (USC), Pt/C electrodes were fabricated by using pulse current electrodeposition methods. With the use of current pulses rather than direct current, a higher deposition current density could be used, and Pt deposits with a higher surface area and activity are possible. Figure 6 compares the performance of USC's electrodeposited catalyst with a loading of 0.15 mg/cm² to commercial ETEK catalyst of 0.4 mg/cm². The kinetic enhancement with the USC catalyst is on the order of 20 mV at all current densities.

USC has identified the optimum current density and the duty cycle for the electrodeposition of higher activity Pt and Pt alloys and is currently fabricating subscale MEAs for testing at UTCFC.

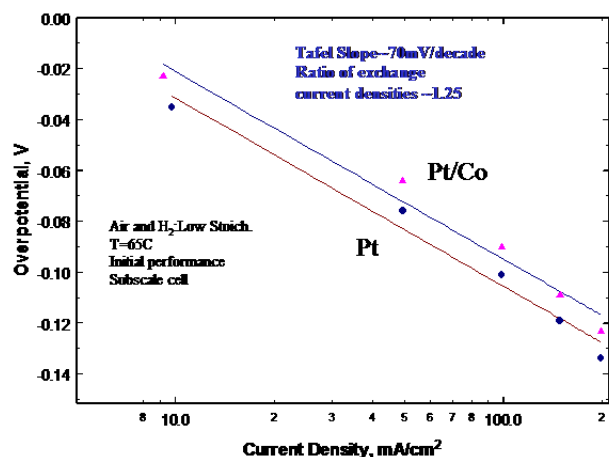


Figure 4. Comparison of the Tafel Behavior for Pt-Co and Pt Catalyst Systems (The kinetic enhancement obtained with Pt-Co is ca. 10 mV at all current densities.)

At UTRC, reproducible and SOA MEAs are being fabricated to aid in the catalyst down-selection process. Performance of some of the sample MEAs fabricated at UTCRC are presented in Table 3. As seen in the table, the air/H₂ performance of the

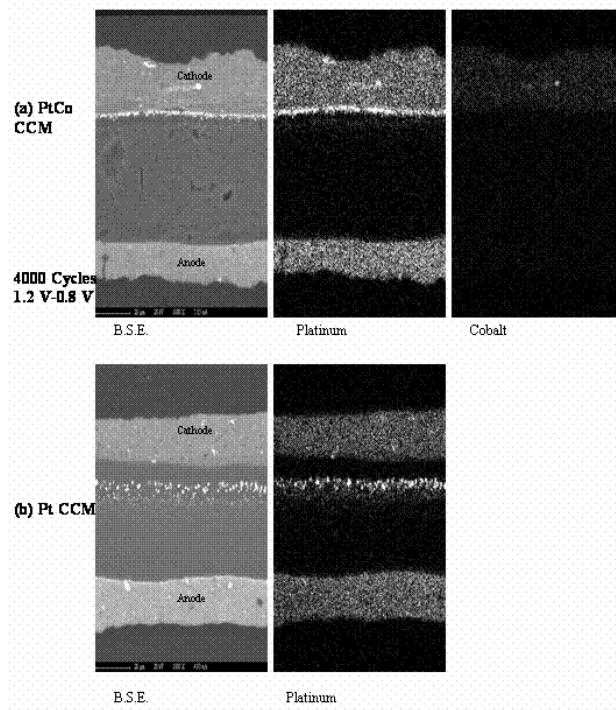


Figure 5. EMPA Images for Pt-Co and Pt Catalysts after 500 hours of Endurance Hold at 0.5 A/cm²

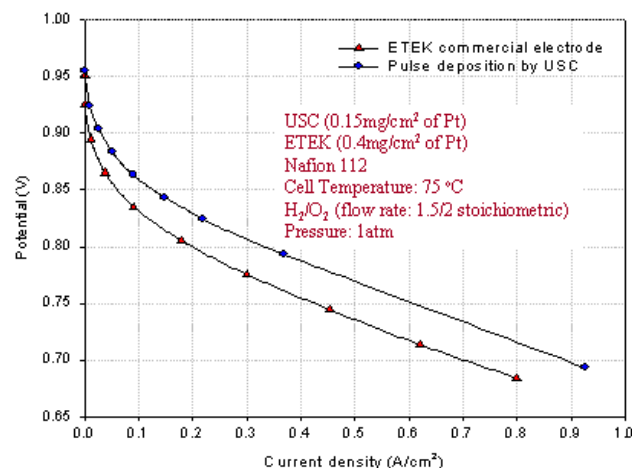


Figure 6. Performance of USC's Electrodeposited Catalyst with a Loading of 0.15 mg/cm² Compared to Commercial ETEK Catalyst of 0.4 mg/cm² (The kinetic enhancement with the USC catalyst is on the order of 20 mV at all current densities.)

UTRC MEAs is comparable to the commercial MEAs, and the performance reproducibility is excellent. Also shown in Table 3 are the DOE targets for the reduced loading. Once the going forward catalyst systems are identified, UTRC will optimize the catalyst layers and aid in the reduction of the Pt loading.

References

1. 2002 UTCFC Annual Report (also the Q1 Progress Report), 6/12/2002.
2. Anderson, A. B., Albu, T. V. Catalytic Effect of Platinum on Oxygen Reduction. An Ab Initio Model Including Electrode Potential Dependence, J. Electrochem Soc., 147, 4229-4238 (2000).
3. Stamenkovic, V., Schimdt, T. J., Ross, P. N. and Markovic, N. M., J. Phys. Chem. B, 106, 11970-11979, 2002.
4. US Patent 4,677,092, US 4,806,515, US 5,013,618, US 4,880,711, US 4,373,014, etc.

Table 3. Performance Comparison of UTRC MEAs

CCM ID	V, mV @ 400 mA/cm ²		V, mV @ 100 mA/cm ²		ECA, m ² /g Pt		Comments
	H ₂ /O ₂	H ₂ /Air	H ₂ /O ₂	H ₂ /Air	Cathode	Anode	
DOE target	0.80		0.85		N/A		Membrane thickness 15µm
REM 411 Commercial	0.824	0.786	0.885	0.857	-	-	Membrane thickness 15µm
REM 404	0.800	0.760	0.875	0.848	46	54	Membrane thickness 15µm
REM 413	0.795	0.757	0.879	0.845	44	69	Membrane thickness 15µm
REM 414	0.790	0.748	0.880	0.848	-	-	Membrane thickness 15µm
REM 415	0.810	0.767	0.887	0.854	54	65	Membrane thickness 15µm
REM 416	0.798	0.756	0.886	0.854	69	44	Membrane thickness 15µm